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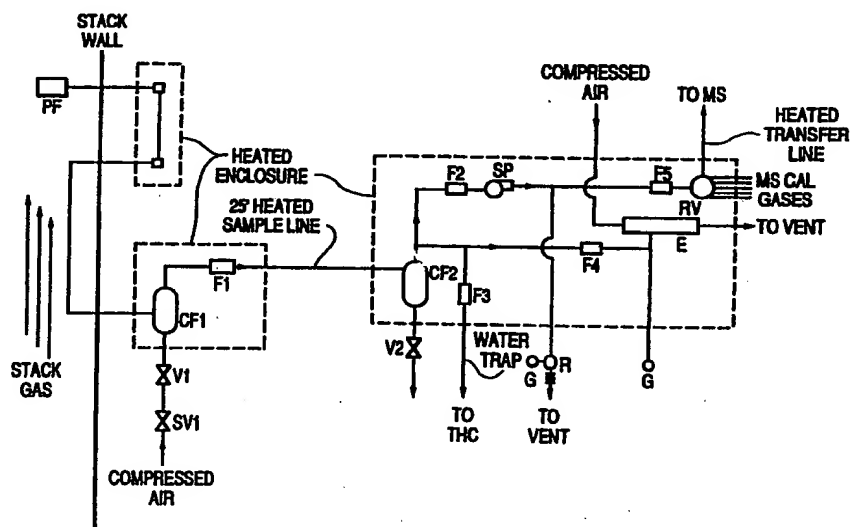
(57) Abstract

A continuous emissions monitoring system for exhaust gas emissions containing HCl comprising a sampling subsystem with a sample probe in the effluent collecting effluent that is transmitted through heated conduits to filtering means and pump means to a mass spectrometer. The sampling subsystem is maintained at a temperature no less than about 190 °C and the flow rate through the system is greater than about 10 liters per minute. The process for continuous monitoring of exhaust emissions containing HCl extracts an exhaust gas sample and maintains the temperature and physical state f the exhaust gas through ut transport of the sample from the exhaust effluent to a mass spectrometer.

+ DESIGNATIONS OF "SU"

Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

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Description

A MASS SPECTROMETER-BASED CONTINUOUS
EMISSIONS MONITORING SYSTEM FOR
HAZARDOUS WASTE STACK GAS MEASUREMENTS

Technical Field

Over the past several years, the need for limiting
stack gas emissions at industrial facilities which process
hazardous waste has become a topic of increasing importance.
Government regulations are now pending for boilers and
industrial furnaces burning hazardous waste as fuels or for
recycling and methodology for continuous emissions monitoring
systems (CEMS) is currently being evaluated.

Background Art

Among the compounds for which emissions limits will be
set are HCl, SO_2 and nitrogen oxides, NO_x. At the present
time, only a limited number of CEMS for HCl are installed in
industrial environments and, as noted by Buonicore in
"Experience with Air Pollution Control Equipment and
Continuous Monitoring Instrumentation on Hazardous Waste
Incinerators," *Journal of Hazardous Materials*, 1989, Vol. 22,
pp. 233-242, the reliability of these systems has yet to be
proven.

In December of 1989, the USEPA requested comments on
"whether continuous emissions monitoring for HCl would be a
feasible, practical requirement in lieu of waste analysis for
chlorine to limit HCl emissions." The ASME Research
Committee on Industrial and Municipal Wastes responded that
only one of five monitoring devices found by the EPA to be
"acceptable" was actually reliable in plant operations. The
Committee noted that service and support on the device, which
is based on infrared technology and produced in West Germany,
has been inadequate to date. The Committee therefore
concluded that continuous monitoring for HCl may be
appropriate at large facilities but is inappropriate at
smaller facilities.

A number of paramet rs in stack gas emissions can be
used to evaluate the totality of the combustion process and
the adequacy of the emission control system. For example the
amounts of O_2, CO_2, SO_2 and nitrogen oxides, NO_x, present
can indicate if the thermal degradation process is complete.
See Oppelt "Incineration of Harzardous Waste, A Critical
Review," *Journal of Air Pollution Control and Waste
Management*, 1987, Vol. 37, No. 5, pp. 558-586, and C. Lee et
al., "An Overview of Harzardous/Toxic Waste Incineration,"
Journal of Air Pollution Control and Waste Management, 1986,
Vol. 36, No. 5, pp. 922-931, for reviews of the usefulness of
these gases as indicators and the CEMS technology currently
available for their measurement.

Products of incomplete combustion (PICs) are also
components in stack gas for which public concern is high due
to their potential toxicity. As noted by K. Lee in "Research
Areas for Improved Incineration System Performance," *Journal
of Air Pollution Control and Waste Management*, 1989, Vol. 38,
No. 12, pp. 1542-1550, their formation and emissions of PICS
are not well understood. Continuous monitors are not yet
commercially available although Overton, "Development of
Real-Time Stack-gas Analysis Methods," *Journal of Hazardous
Materials*, 1989, Vol. 22, pp. 187-194, recently reported on a
microbore gas chromatographic method which appears promising.

Continuous data for SO_2 and HCl emissions can help
insure that these gases are adequately neutralized by the
scrubbing system. As noted by Podlenski in "Feasibility
Study for Adapting Present Combustion Source Continuous
Monitoring Systems to Hazardous Waste Incinerators," *EPA
Report No. 600/8-84-011a*, 1984, such data can provide
information that can be used as a guide for design and
operation purposes. At the present time, however, the EPA
accepted technology for HCl monitoring is a manual sampling
method with subsequent laboratory analysis by eith r
titration or ion chromatography.

In order to improv performance at industrial
facilities processing hazardous waste and to monitor stack

gas emissions for the purpose of risk assessment, there has
been a longstanding need for a CEMS which efficiently
monitors exhaust gases, especially HCl.

A CEMS consists of two major subsystems, an analytical
subsystem and a sample extraction subsystem, each of which
must be considered in the development of a complete system
for continuous stack gas measurement. A variety of
analytical technologies including gas chromatography, fourier
transform infrared spectroscopy, photoacoustic spectroscopy,
ion mobility spectrometry and mass spectrometry were
evaluated and a commercially available mass spectrometer was
chosen as the analytical subsystem. The advantages and
disadvantages of the technologies mentioned above for this
intended purpose has been discussed by Harlow et al., "Design
of a Continuous Emissions Monitoring System at a
Manufacturing Facility Recycling Hazardous Waste,"
*Proceedings, Hazardous Materials Control Research Institute,
Great Lakes 90, Cleveland, OH*, pp. 285-289, 1990.

As noted previously, use of CEMS to monitor compounds
such as O_2 and nitrogen oxides, NO_x is known. These
compounds can be delivered to an analytical instrument while
allowing the stack gas to cool since they are gases at
routine ambient temperatures. In addition, none of these
substances are very reactive, making sample extraction
systems for these compounds relatively straightforward.
There is no need for a heated system and most particulate
material is removed with the water. However, conventional
CEMS sample extraction is unsatisfactory for compounds such
as HCl.

Disclosure of the Invention

The objective of this invention is to provide a mass
spectrometer-based continuous emissions monitor with a heated
sample extraction system. A further object of the present
invention is to provide CEMS capable of continuous
measurement of at least O_2, CO_2, SO_2, NO_x, and HCl.
Another object of the present invention is to develop a
heated sample extraction subsystem that would keep HCl in the

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vapor phase, prevent corrosion and minimize problems associated with the reactive nature of HCl.

One embodiment of the present invention is a process for continuously monitoring the gaseous exhaust of an effluent stream containing HCl. The process comprises the steps of: extracting a sample of a gaseous effluent from an effluent stream; transporting the sample in a sample line within the effluent stream to maintain the sample at the desired sample temperature; hot filtering the sample; transferring the filtered sample through a heated transfer line to a heated analyzing station; maintaining a flow rate of the filtered sample of at least 10 liters per minute; and analyzing the filtered sample by mass spectrometry. Throughout the entire process the sample is maintained at a temperature no less than about 190°C.

Another embodiment of the present invention is a system for providing compositionally representative samples of the gaseous component of an effluent stream consisting of a mixture of gas, vapor and particulate material. The system comprises a sampling means within the effluent stream for continuously extracting samples of that stream; a conduit in flow communication with the sampling means, the conduit is heated by the effluent stream; a heated filtering system in flow communication with the conduit, the filtering system removes particulates from the samples; at least one heated transfer line in flow communication with the heated filtering system; an analyzer in flow communication with the transfer line, the analyzer comprises a heated sample pump and a heated capillary stem for sample introduction into a mass spectrometer, the pump is located in close proximity and upstream from the capillary stem and maintains a flow rate of at least 10 liters per minute within the sampling system. The sampling system, conduit, heated filtering system, heated transfer line and the sample pump are maintained at a temperature of not less than about 190° C.

A third embodim nt of this invention is a continuous emissions monitoring system comprising the heated sampling system described above and a mass spectrometer.

Brief Description of the Drawings

Figure 1 is a schematic drawing of the sample extraction subsystem according to a preferred embodiment of the invention.

Figure 2 shows the improvement in HCl response of the mass spectrometer after the above modifications.

Figure 3 is a detail drawing of (a) the probe connection in the sample extraction subsystem and (b) of a standard gas connection in the sample extraction system used for calibration.

Figure 4 is a plot of O_2 and HCl concentration versus time obtained while conducting the calibration error tests of Example 1.

Figure 5a shows the O_2 and HCl response curves when switching from blowback air to exhaust stack gas prior to modification for HCl analysis.

Figure 5b shows the O_2 and HCl response curves when switching from blowback air to exhaust stack gas after modification for HCl analysis.

Figure 6 is a plot of HCl gas concentration and percent error from the data obtained in the relative accuracy tests of the present invention in Example 2.

Best Mode for Carrying Out the Invention

The mass spectrometer-based continuous emissions monitoring system (CEMS) has two subsystems, the sample extraction subsystem and the mass spectrometer subsystem. The mass spectrometer subs stem, which measures the percent concentration of individua components of the stack gas sample, consists of the mass spectrometer hardware and the data acquisition equipment. The sample extraction subsystem's function is to d liv r the stack gas sample to the mass spectrometer without changing the stat or

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composition of th gaseous and vapor portions of the
extracted sample.

Sample Extraction Subsystem

The design criteria for the sample extraction subsystem
included:

1)   heating of the system in its entirety to avoid
      water condensation with subsequent loss of HCl;

2)   adequate filtration to remove particulate
      material larger than one micron;

3)   a pumping system with sufficient capacity to draw
      the sample from the stack with minimum delay
      time; and

4)   ease of maintenance.

Figure 1 shows a schematic of the preferred sample
extraction system of this invention. A sampling means,
preferably a sample probe consisting of a 30 micron filter
mounted on a stainless steel tube, is installed inside the
exhaust stack approximately 8 stack diameters downstream from
the input conduits of the fans driving the effluent through
the exhaust stack, and 8 stack diameters upstream from the
effluent exhaust at the end of the stack. A sample line then
runs through the exhaust stack and within the effluent to
allow the heat of the exhaust stack to maintain the desired
sample temperature, thus eliminating the need for a long
transfer line that must be heated and maintained. The sample
line may first run from the sampling means to a heated
maintenance enclosure mounted on the exhaust stack wall which
facilitates maintenance of the probe and provides a point for
connection of standard gases used in calibration and testing.

At the base of the stack the exhaust sample line enters
a second heated enclosure which houses a series of filters
comprising a first filter, preferably a cyclone filter, to
remove large particulates and a secondary filter, preferably
a c ramic glass microfiber filter, to remove small
particulates. Small particulat s are those having sizes less
than about 5 microns to about 0.1 micron. A source of
compressed air may be connect d to the first filter to

blowback the system periodically to avoid sample line and
filter blockage. The exhaust gas sample then passes through
a heated transfer line to a heated analyzing station.

The heated analyzing station comprises a pump,
preferably an eductor, is used to move at least 10 liters per
minute, preferably about 15 liters per minute, of the exhaust
gas sample from the stack to the enclosure upstream from mass
spectrometer, and a heated capillary for sample introduction
into the mass spectrometer. The analyzing station may also
contain a second series of filters to further remove
particulate material. Preferably the second series of
filters comprises a cyclone filter to remove large
particulates and a second ceramic filter to remove small
particulates. Only particles smaller than 0.1 micron pass
the final filter. After filtration, the exhaust gas sample
may be split and directed to a total hydrocarbon analyzer. A
second pump, preferably a diaphragm pump equipped with a
backpressure regulator at the outlet side of the pump,
insures that an appropriate flow of sample is delivered to
the mass spectrometer. The filtered exhaust gas sample may
be connected to the mass spectrometer via computer-controlled
16 position rotary valve which may also have connections to
mass spectrometer calibration gases.

To accurately analyze for HCl it is critical to
maintain the sample at the appropriate elevated temperature.
The slightest cold spot that allows condensation of water not
only removes HCl but causes particulate to drop out of the
gas stream with subsequent blockage. For analysis of HCl,
the system is heated to a temperature no less than about
190°C. In addition, HCl is an extremely reactive substance
which can lead to corrosion. The elevated temperatures,
which insure that HCl remains in the vapor phase, eliminates
corrosion problems.

The reactive nature of HCl can lead to "wall affects",
th adsorption to and desorption from surfaces. Construction
materials are therefore an important c nsideration in
minimizing these affects. Pref rably materials such as

teflon and stainless material are us d as they show the least propensity to adsorb HCl.

The following changes are preferably made to the mass spectrometer to reduce HCl adsorption and improve response. First, the rotary valve rotor and a mass spectrometer ferrule, ordinarily made of a graphite and vespel composite, are replaced with components made of teflon. Next, the mass spectrometer's ionizer, which has a large surface area, is replaced with an "open" ionizer constructed of wire mesh in an effort to reduce the surface area available in the mass spectrometer to adsorb/desorb HCl.

Figure 2 shows the improvement in HCl response of the mass spectrometer after the above modifications. The lower curve labelled "Initial" is the response prior to modification. The middle curve labelled "Teflon" shows the improvement with a change of material. The upper curve labelled "Open Ionizer" shows the improved response with the open screen-type ionizer.

Sample flow rate also appears to have a dramatic effect on the adsorption of HCl. It had been reported by Nelson that HCl has a tendency to adsorb on material surfaces at flow rates less than 10 liters per minute. See Nelson, "Continuous Measurement of HCl Emissions from MSW Incineration Facilities," *Proceedings, Air Pollution Control Association International Speciality Conference on the Thermal Treatment of Municipal, Industrial and Hospital Waste*, Pittsburgh, PA., p. 183 (1987).

Although the flow from the sample source in the exhaust stack to the outlet of the diaphragm pump was 15 liters per minute, the flow dropped dramatically at the rotary valve. Therefore, the fused silica capillary inlet of the mass spectrometer was moved from the common outlet of the rotary valve to the outlet of the diaphragm pump where flow rates are high. In the present invention flow rat s greater than about 10 liters per minute, preferably about 15 liters per minut , which show a lower tendency for adsorption, are employed.

Relative accuracy tests for HCl wer repeated with the
modified instrument and inlet configuration. The data in
Table 6 show that the relative accuracy for HCl obtained with
the new configuration was 5.8%, well within the EPA
requirement and more in line with the accuracies obtained for
the other gases tested.

Mass Spectrometer Subsystem

The mass spectrometer used in the invention is a
process mass spectrometer which continuously introduces the
gas stream directly into the analyzer and monitors specific
ion intensities for each component in the stream. A
preferable mass spectrometer is a Questor Process Analyzer
manufactured by Extel Corporation of Pittsburgh,
Pennsylvania.

When the sample enters the mass spectrometer's vacuum
chamber, it flows through a region referred to as an electron
impact ion volume. Some percentage of the sample molecules
collide with electrons thereby producing positively charged
molecular ions and fragment ions. The ions thus formed are
electrically removed form the ion region using a series of
lenses and are "shot" into the quadrupole mass filter which
separates the ions according to their mass-to-charge ratio.
A mass spectrum, a plot of ion intensity versus mass-to-
charge ratio, for every component is unique. In process mass
spectrometry, a single ion is chosen for each component to be
analyzed. In situations where the ion intensity is the
result of several components in the stream, the component of
interest is resolved mathematically by subtraction of the
interfering components' ion intensities.

The components to be monitored are easily selected
using the mass spectrometer's data system to create an
"analysis method". In the present invention, the instrument
is preferably set to continuously monitor SO_2, nitrogen
oxides (as NO), HCl, Cl_2, N_2, O_2, CO_2 and Ar. An
analysis of the eight compon nts is completed ev ry three
seconds with the data reported locally and sent to the plant
control computer. The instrument automatically calibrates

itself using certifi d standard blends which are connected to
the rotary valve. The calibration routine takes
approximately ten minutes to complete.

Reliability

　　　　Maintenance on the CEMS of the present invention is
minimal. The mass spectrometer requires only routine
cleaning and maintenance. The sample extraction system show
no signs of corrosion during the period in which it was
developed and tested and requires minimal maintenance
consisting of daily blowback and periodic changes of the
system filters. Filter changes are required two to three
times monthly and take approximately one hour.

　　　　The following examples are intended to illustrate, not
limit, the present invention.

EXAMPLES

　　　　These examples compare and contrast the present
invention with and without the modifications described above
for HCl analysis. Example 1 was conducted without those
modifications. Example 2 presents results obtained with the
modified system.

　　　　The calibration drift, calibration error and relative
accuracy (RA) test methods used in these examples are
outlined by the Environmental Protection Agency in 40 CFR
(Part 60, Appendix B, Specifications 3 and 4) and an EPA
draft performance specification for HCl. These methods are
summarized briefly below.

Sample Introduction

　　　　Standard gases are introduced in two ways. First, for
direct mass spectrometer introduction, cylinders were
connected to the rotary valve (see Figure 1) to introduce gas
directly to the mass spectrometer. Introduction at this
point bypasses all portions of the extraction system used for
sample acquisition and conditioning and demonstrates the mass
sp ctrometer's capabilities. Second, for introduction
through the sampl extraction system, standard gas cylinders
are introduced at the maintenance nclosure for the probe.
Figure 3a shows the normal probe connection at the stack.

For th tests conducted to assess sample system performance, the probe filter was disconn cted and a tee inserted in its place (Figure 3b). A standard gas cylinder was connected to one side of the tee and the cylinder pressure adjusted until there was gas flowing out of the tee at atmospheric pressure. This insured adequate sample for the sample extraction system without pressurizing the system.

Calibration Drift Test

The calibration drift test measures the stability of the CEMS calibration over time. The test is performed on both zero and high level standards. After instrument calibration, standards are introduced though the sample extraction system and a zero time measurement taken. After 24 hours, during which no maintenance, repair or adjustment took place, the standards are again introduced and a second measurement taken, the 24-hour reading. After the 24-hour measurement, the instrument is calibrated and the next 0-time measurement taken. The test is generally repeated for seven consecutive days.

For each 24-hour period, the calibration drift is calculated by the equation:

$$\text{Calibration drift} = \frac{d}{\text{span value}} \times 100$$

where d = (0-time measurement) - (24-hour measurement)

span value = the upper limit of the CEMS measurement
             range specified for the facility.

Calibration Error Test

The calibration error test is designed to assess the accuracy and linearity of the CEMS over the entire measurement range. After instrument calibration on a concentration equal to the span value, zero, mid and high level standards are each introduced three times through the sample extraction system.

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The calibration error is calculat d by th equation:

$$\text{Calibration error} = \left| \frac{d}{\text{span value}} \right| \times 100$$

where $\bar{d}$ = mean difference between the CEMS response and the known reference concentration.

Relative Accuracy

The relative accuracy test is used to validate the calibration technique and verify the ability of the CEMS to provide representative and accurate measurements. The CEMS measurement is compared to a reference measurement obtained using an EPA accepted Performance Test Method (PTM). A minimum of nine tests is generally performed for each compound evaluated.

The relative accuracy is calculated by the equation:

$$\text{Relative Accuracy} = \frac{|\bar{d}| + |cc|}{\overline{\text{PTM}}} \times 100$$

where $|\bar{d}|$ = absolute value of the mean of the differences of the CEMS and PTM measurements

$|cc|$ = absolute value of the confidence coefficient
= $t_{0.976} \dfrac{S_d}{\sqrt{n}}$

$\overline{\text{PTM}}$ = average reference measurement

EXAMPLE 1

In this example, only O_2, CO_2 and SO_2 were evaluated using a CEMS without the system modifications needed to ensure accurate HCl measurement as described above. As shown by the results below the system configuration used for these experiments was not adequate for accurately measuring HCl.

CEMS Configuration

Only O_2, CO_2 and SO_2 wer evaluated since certifi d HCl standards were not available du to long delivery times from th gas manufacturer. Table 1 shows the comparison of

the standard d viations (r peatability) obtained by introducing standards directly to the mass spectrometer and through the sample extraction system. The data compare well showing that the sample extraction system causes no degradation of the mass spectrometer response.

Table 1
Repeatability

	% Conc.	Direct Introduction Std. Dev.	% RSD	Through Sample Std. Dev	System % RSD
O_2	8.438	0.009	0.11	0.012	0.15
CO_2	5.259	0.009	0.16	0.008	0.15
SO_2	0.102	0.002	0.26	0.001	0.23

$$\% \text{ RSD} = \frac{\text{Std. Dev.}}{\% \text{ Conc.}} \times 100$$

A calibration drift test was performed to measure the stability of the CEMS calibration over time. The results in Table 2 show that the average calibration drift for O_2, CO_2, and SO_2 for the seven measurements was at least a factor of ten better than the EPA requirement.

TABLE 2
Calibration Drift Tests

Compound	% Conc. Tested	Average MS Drift	EPA Requirement
O_2	0.00	0.02	0.5% from reference
O_2	18.11	0.04	0.5% from reference
CO_2	0.00	0.00	0.5% from reference
CO_2	11.21	0.05	0.5% from reference
SO_2	0.00	0.02	2.5% of span
SO^2	0.248	0.04	2.5% of span

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A calibration error test was conducted for O_2, CO_2, and SO_2 and HCl to assess the accuracy and linearity of the CEMS over the entire measurement range. The results in Table 3 show that the calibration errors for all components meet the EPA specification when calculated using the EPA formula. However, the calibration error for HCl is significantly higher than the errors for O_2, CO_2, and SO_2.

TABLE 3

Calibration Error Tests

Compound	% Conc. Tested	MS Error %Span	EPA Requirement
O_2	0.00	0.03	Not required
O_2	8.40	0.11	Not required
O_2	18.11	0.08	Not required
CO_2	0.00	0.03	Not required
CO_2	5.35	0.76	Not required
CO_2	11.21	0.13	Not required
SO_2	0.00	0.22	Not required
SO_2	0.103	0.00	Not required
SO_2	0.248	0.44	Not required
HCl	0.00	3.3	5.0% of span
HCl	0.0596	2.1	5.0% of span
HCl	0.1560	2.1	5.0% of span

Table 4a shows the mass spectrometer response for direct introduction of the mid level standards for HCl and O_2. In both cases, th errors are quite small, although it was noted that HCl took considerably more tim to equilibrate to the certified value than O_2.

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Table 4a
Calibration Error
Standards Introduced Directly to the MS

Component	Certified Value	Measured Value	d	% Error
O$_2$ (% Conc.)	8.40	8.44	0.04	0.48
HCL	596	593	3	0.50

Table 4b gives the data obtained during the calibration error test when standards were introduced through the sample extraction system.

Table 4b
Calibration Error
Standards Introduced through the Sample Extraction System

Component	Certified Value	Measured Value	d	% Error	Change Made
O$_2$ (% Conc.)	8.40	8.42	0.02	0.24	Zero-Mid
O$_2$	8.40	8.44	0.04	0.48	High-Mid
O$_2$	8.40	8.42	0.02	0.24	Zero-Mid
HCl (ppm)	596	475	121	20.3	Zero-Mid
HCl	596	679	83	13.9	High-Mid
HCl	596	509	87	14.6	Zero-Mid

The O$_2$ data compare well to that obtained with direct introduction. The HCl data is very poor by comparison and appears to be dependent upon the last gas analyzed. For example, when changing from the zero gas to the mid standard, the measured reading was low whereas the measured reading was high when changing from the high to mid standard.

A plot of O$_2$ and HCl concentration versus time obtained while conducting the calibration error tests is shown in Figure 4 and furth r confirm d th system's sluggish response to HCl. The pl t shows the mass spectrometer response when introducing the mid level and high level standards. Each data point is a one minute average of the

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mass spectrometer response. O_2 responded to the change in
the gas standard within one minute and equilibrated to the
certified concentration in less than three minutes whereas
HCl had not equilibrated to the certified value after flowing
the standard for 15 minutes.

Relative accuracy tests, designed to verify the ability
of the CEMS to provide representative and accurate
measurements, were conducted to further assess the CEMS'
capability to analyze the gases of interest. The results in
Table 5 show that O_2, CO_2, and SO_2 were well within the
limits set by the EPA.

Table 5
Relative Accuracy Tests
Original CEMS Configuration

Compound	MS %RA	EPA Requirement
O_2	3.8	20.0
CO_2	2.5	20.0
SO_2	5.8	20.0
HCL	22.1	20.0

EXAMPLE 2

The following tests were performed with the modifica-
tions for HCl analysis described above.

Figure 5a shows the O_2 and HCl response curves when
switching from blowback air to stack gas. The O_2 and HCl
delay times were 36 and 45 seconds, respectively. O_2
equilibrated within approximately 75 seconds but HCl had not
equilibrated by 93 seconds. Figure 5b shows that with the
modifications to the position of the fused silica capillary
inlet described above the delay time for both O_2 and HCl was
27 seconds and that O_2 and HCl reached equilibrium within 39
and 54 seconds, resp ctively.

Relative accuracy tests for HCl were repeated with th
modified instrument and inl t configuration. The data in
Tabl 6 show that the relative accuracy for HCl obtained with
the new configuration was 5.8%, well within the EPA

requirement and mor in line with the accuracies obtained for the other gases tested. There is, however, a wide variation in % error with two samples having an error as low as 0.4% to the highest error of 10.9%.

TABLE 6

HCl Relative Accuracy

Run %	PTM (ppm)	MS (ppm)	d (ppm)	% Error
1	546	525	21	3.8
2	650	712	-62	9.5
3	721	800	-79	10.9
4	731	671	60	8.2
5	845	821	24	2.8
6	921	1009	4	0.4
7	1101	1097	4	0.4
8	1377	1382	-5	0.4
9	1385	1327	58	4.2

% RA = 5.8%

If the slower response time for HCl were related to higher % errors in the relative accuracy data, one would expect a high % error to occur when the concentration of HCl was rapidly changing during the sampling period and a low % error to be obtained when HCl concentration was relatively stable. Figure 6 is a plot of HCl concentration during the periods of each relative accuracy test with a bar to indicate the % error obtained for that sample. There appears to be little correlation between the % error and concentration stability. Runs #7 and 8 had the lowest % error but were taken during a period when HCl concentration changed dramatically whereas Run #4, for example, shows a much more stable level of HCl but a much higher % error. During these relative accuracy tests, there was a significant problem with leaks at th ground glass joints of the imping rs used to

collect the stack gas for th performance t st measurement
which may have given rise to the variable % errors.

The results obtained in Examples 1 and 2 for the
relative accuracy tests for O_2, CO_2, and SO_2 and HCl were
well within the limits required by the EPA, indicating that a
mass spectrometer with a carefully designed and implemented
sample extraction appears to be viable alternative for
continuous monitoring of stack gas emissions.

The present invention has been disclosed in terms of a
preferred embodiment, however, the scope of the invention is
not limited to this embodiment. The scope of the invention
is determined solely by the appended claims and their
equivalents.

Claims

1.   A process for continuously monitoring the gaseous exhaust of an effluent stream containing HCl, said process comprising,

      extracting a sample of said exhaust from said effluent stream;

      transporting said sample in a sample line within said effluent stream to heat said sample to the desired sample temperature;

      hot filtering said sample;

      transferring said sample through a heated transfer line to a heated analyzing station;

      maintaining a flow rate of said sample of at least 10 liters per minute; and

      analyzing said sample by mass spectrometry;

      wherein said sample is maintained at a temperature no less than about 190°C.

2.   The process of claim 1 wherein said hot filtering step comprises filtration through a series of filters comprising a first filter to remove large particulates and a second filter to remove small particulates.

3.   The process of claim 2 further comprising a second filtration step after said transferring step wherein said sample is passed through a second series of filters located within said analyzing station and which comprises a first filter to remove large particulates and a second filter to remove small particulates.

4.   The processes of claim 3 further comprising a step, prior to said analyzing step, of splitting said sample into two portions and directing the first portion to a mass spectrometer and directing the second portion to a total hydrocarbon analyzer.

5.   The process of claim 4 wherein the analyzing st p continuously monitors SO_2, NO, HCl, Cl_2, N_2, O_2, CO_2 and Ar.

6.   The process of claim 1 wherein the analyzing step
continuously monitors SO_2, NO, HCl, Cl_2, N_2, O_2, CO_2 and
Ar.

7.   A system for providing compositionally
representative samples of the gaseous component of an
effluent stream consisting of a mixture of gas, vapor and
particulate material, said system comprising:

        sampling means within said effluent stream for
continuously extracting samples of said stream;

        conduit means in flow communication with said
sampling means, said conduit means being heated by said
effluent stream;

        heated filtering means in flow communication with
said conduit means, said filtering means disposed to remove
particulates from said samples;

        at least one heated transfer line in flow
communication with said heated filtering means;

        analyzing means in flow communication with said
transfer line, said analyzing means comprised of a heated
sample pump and a heated capillary for sample introduction
into a mass spectrometer, said pump being located in close
proximity to and upstream from said capillary, said pump
maintaining a flow rate of at least 10 liters per minute
within said system,

        wherein said sampling means, conduit means,
heated filtering means, heated transfer line and said pump
are maintained at a temperature of not less than about
190° C.

8.   The system of claim 7 wherein said pump maintains
a flow rate of at least about 15 liters per minute.

9.   The system of claim 7 wherein said sampling means
is comprised of a 30 micron filter mounted on a metal
conduit.

10.   The system of claim 7 wh r in said effluent is
conducted through a stack by means of at least on fan, said
fan inputting effluent into said stack at a fan inlet, said

sampling means being located approximately 8 stack diam ters
downstream from said fan inlet.

11.   The system of claim 7 wherein said effluent is
conducted through a stack by means of at least one fan, said
stack having an exhaust end, said sampling means being
located approximately 8 stack diameters upstream from the
exhaust end of said stack.

12.   The system of claim 7 wherein said system
includes a heated enclosure between said sampling means and
said heated filtering means, said enclosure including means
for providing maintenance to said sampling means.

13.   The system of claim 12 wherein said heated
enclosure between said sampling means and said heated
filtering means includes means for injecting gas into said
system in a direction opposite to flow of samples through
said system.

14.   The system of claim 7 wherein said system
includes a heated enclosure between said sampling means and
said heated filtering means, said enclosure including means
for injecting calibration gases into said system proximate
said sampling means.

15.   A continuous emissions monitoring system
comprising the system of claim 7 and a mass spectrometer
which includes a mesh type ionizing screen.

16.   The system of claim 7 wherein said system
includes a computer controlled multiport valve in flow
communication with said mass spectrometer, wherein said
multiport valve is constructed of stainless steel and teflon.
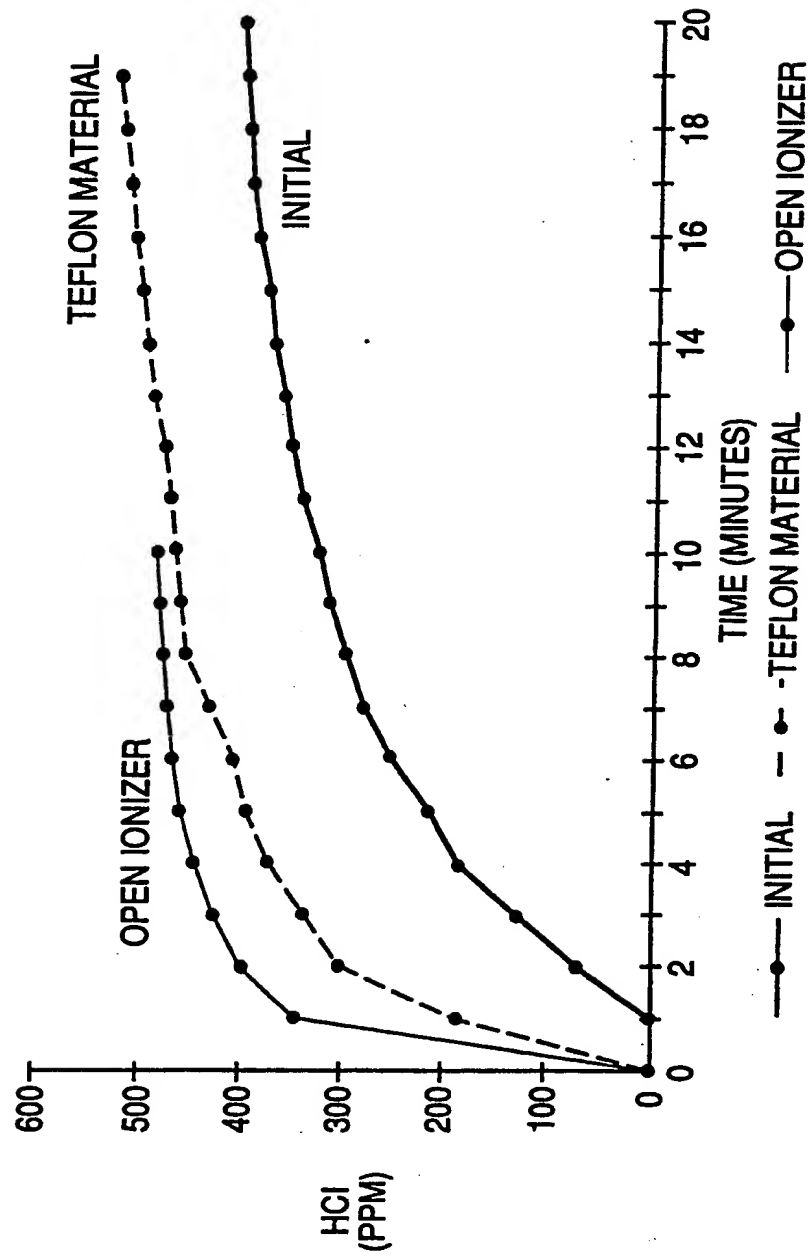
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FIG. 1
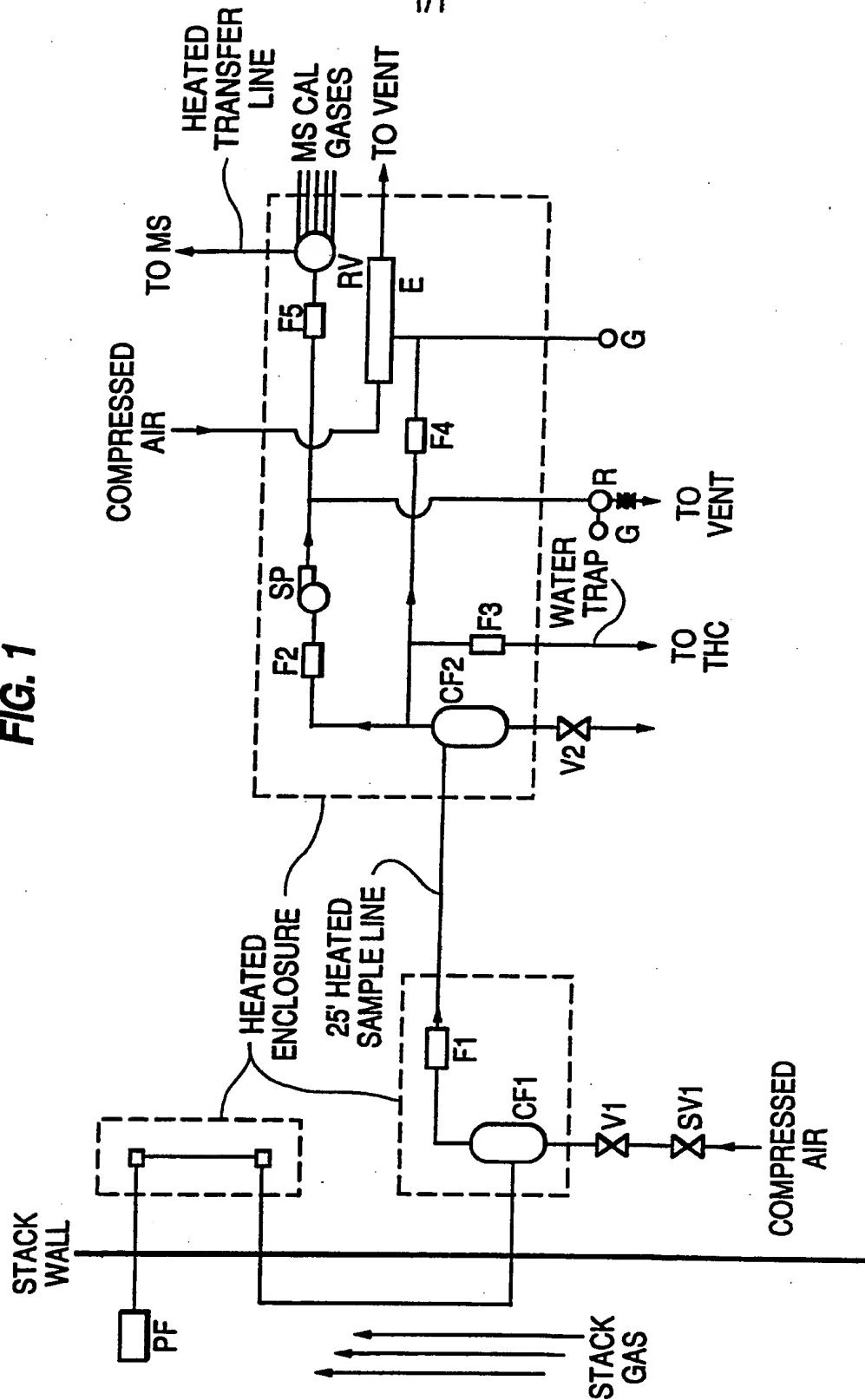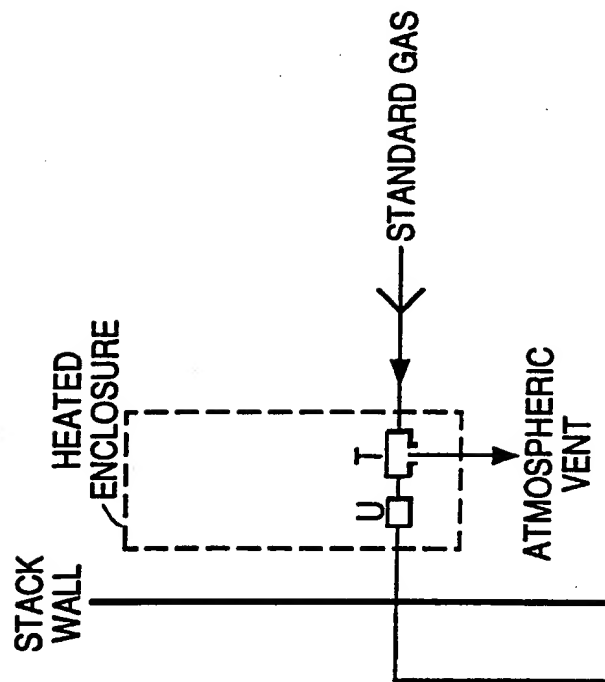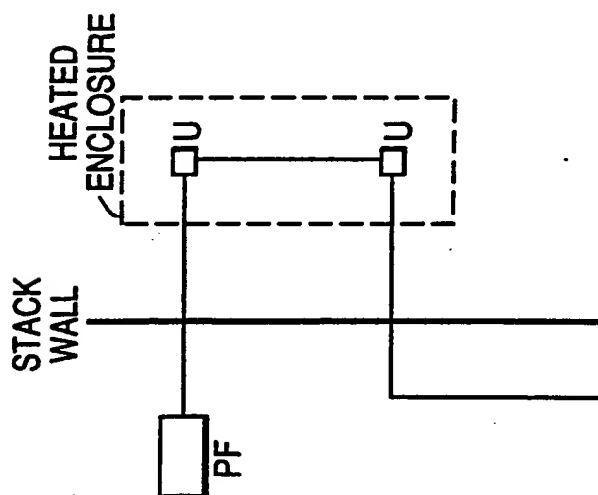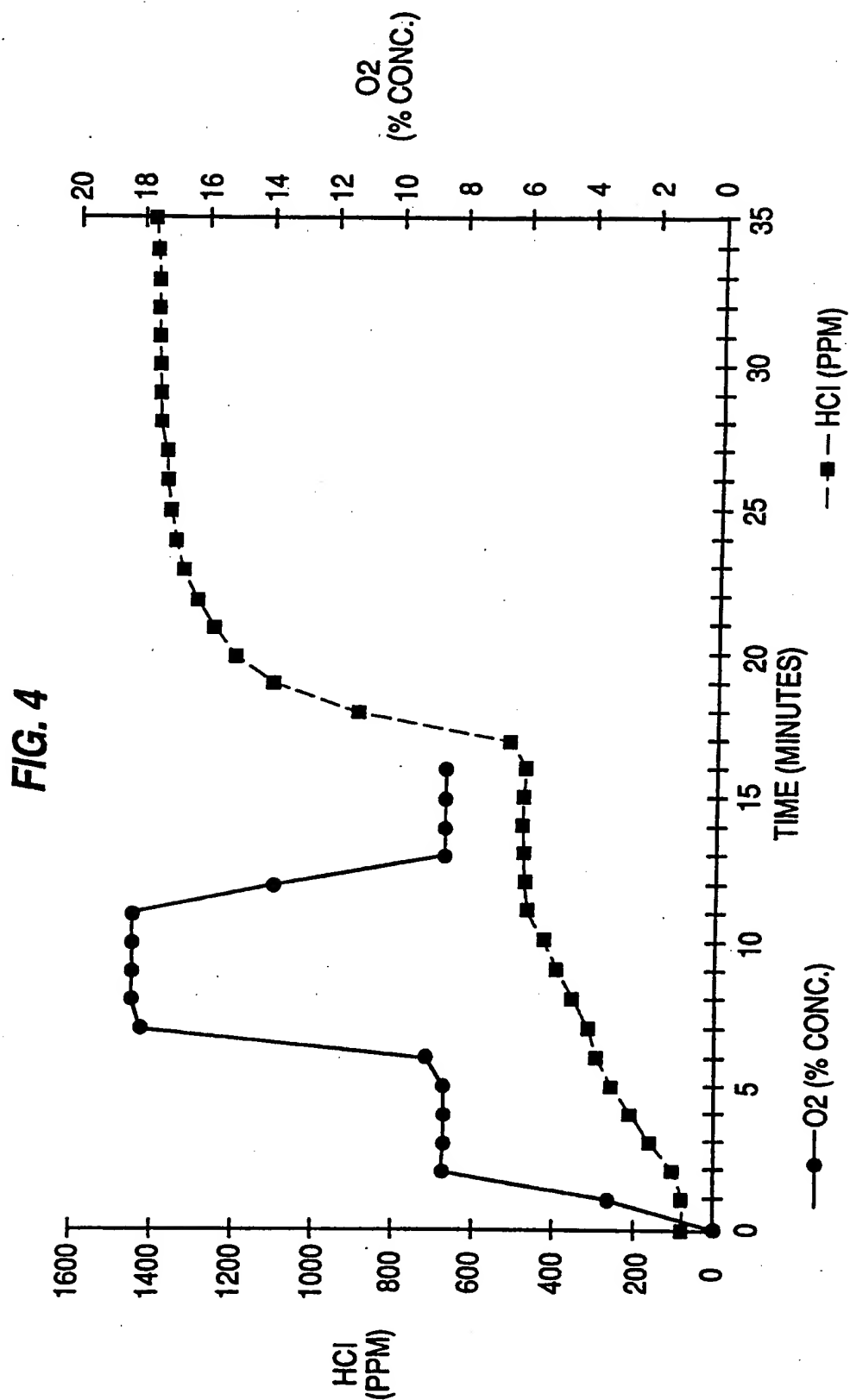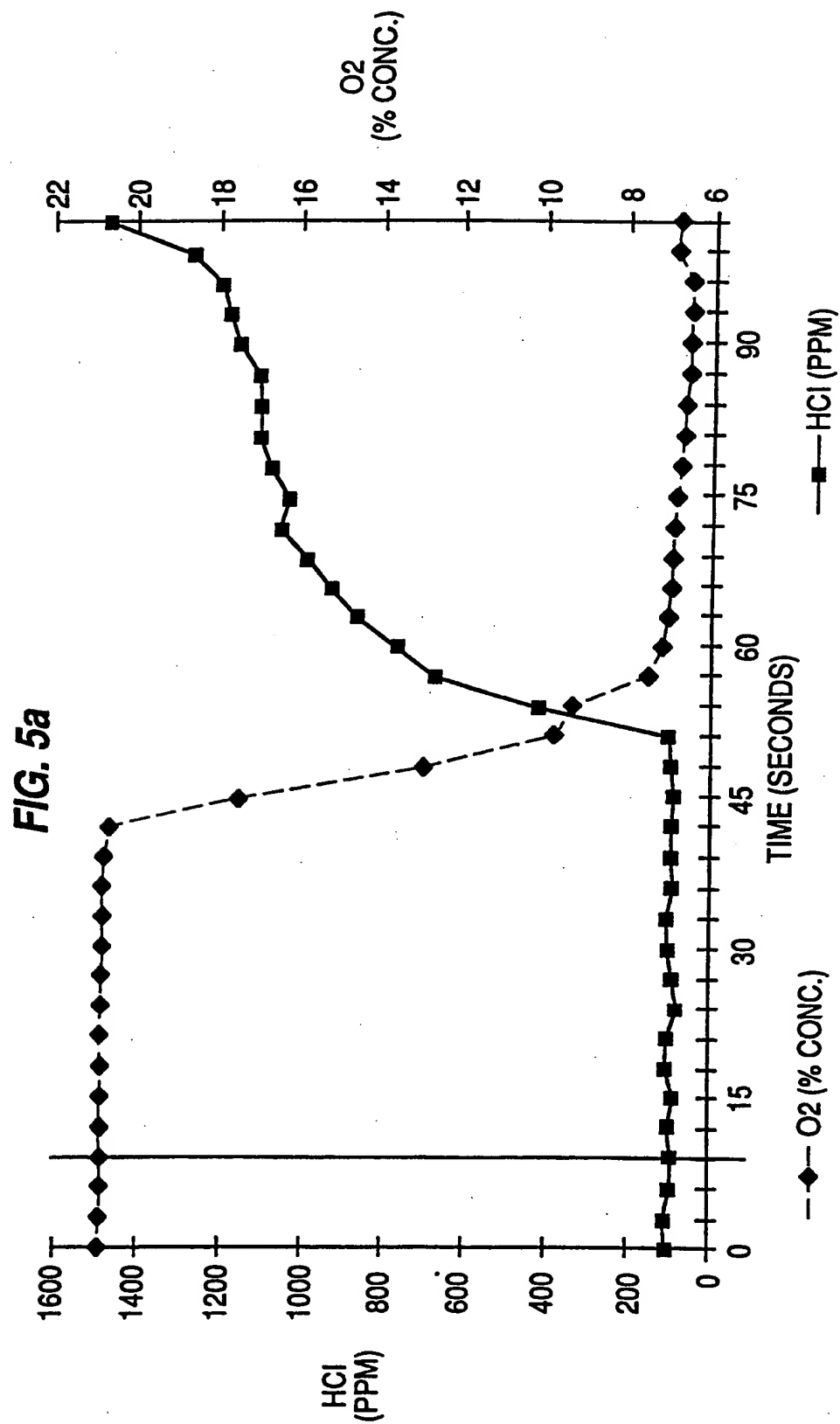
FIG. 2

FIG. 3b

FIG. 3a

FIG. 4

O2
(% CONC.)

TIME (MINUTES)

HCl (PPM)

HCl
(PPM)

— ■ — HCl (PPM)

— ● — O2 (% CONC.)

FIG. 5a

FIG. 5b

FIG. 6

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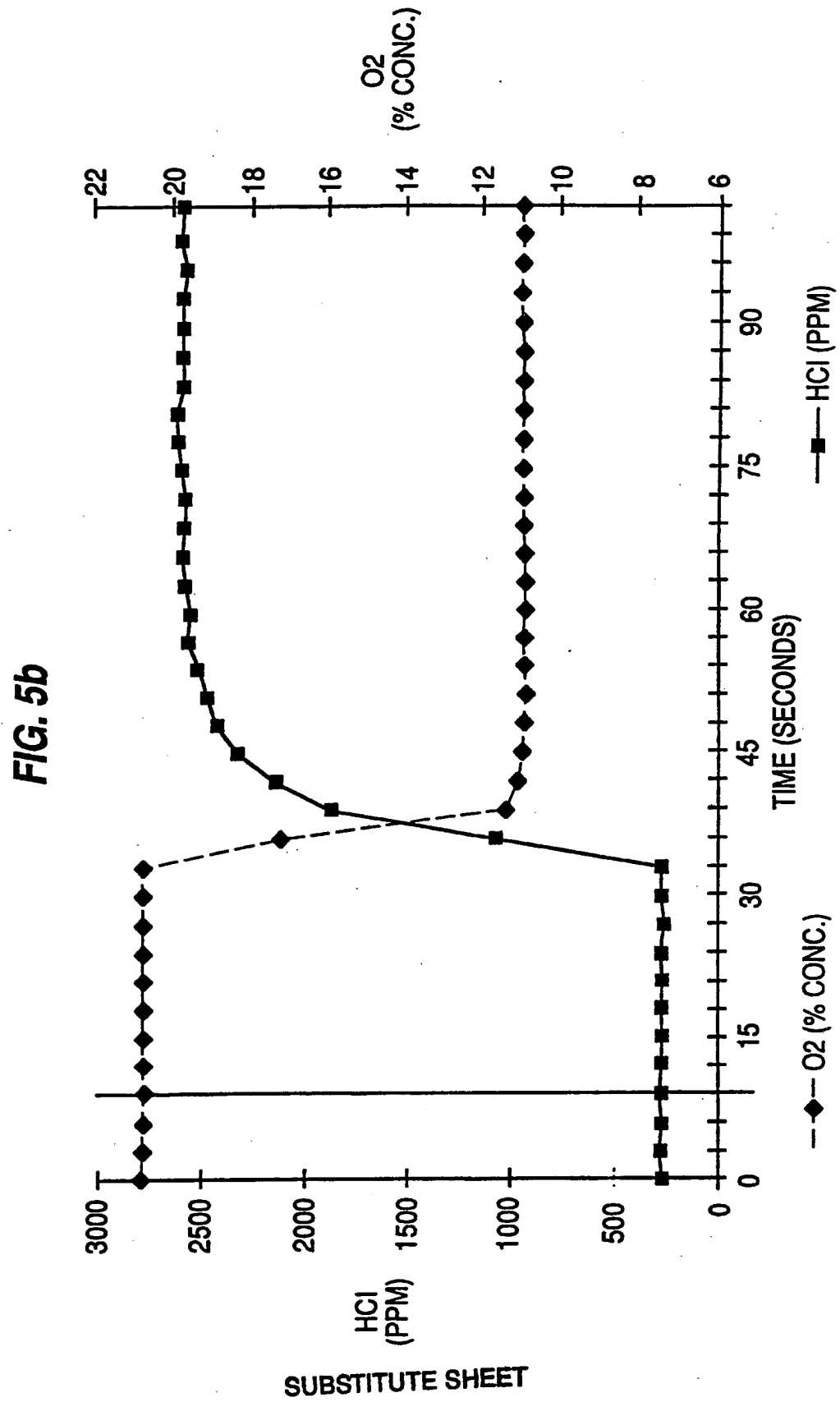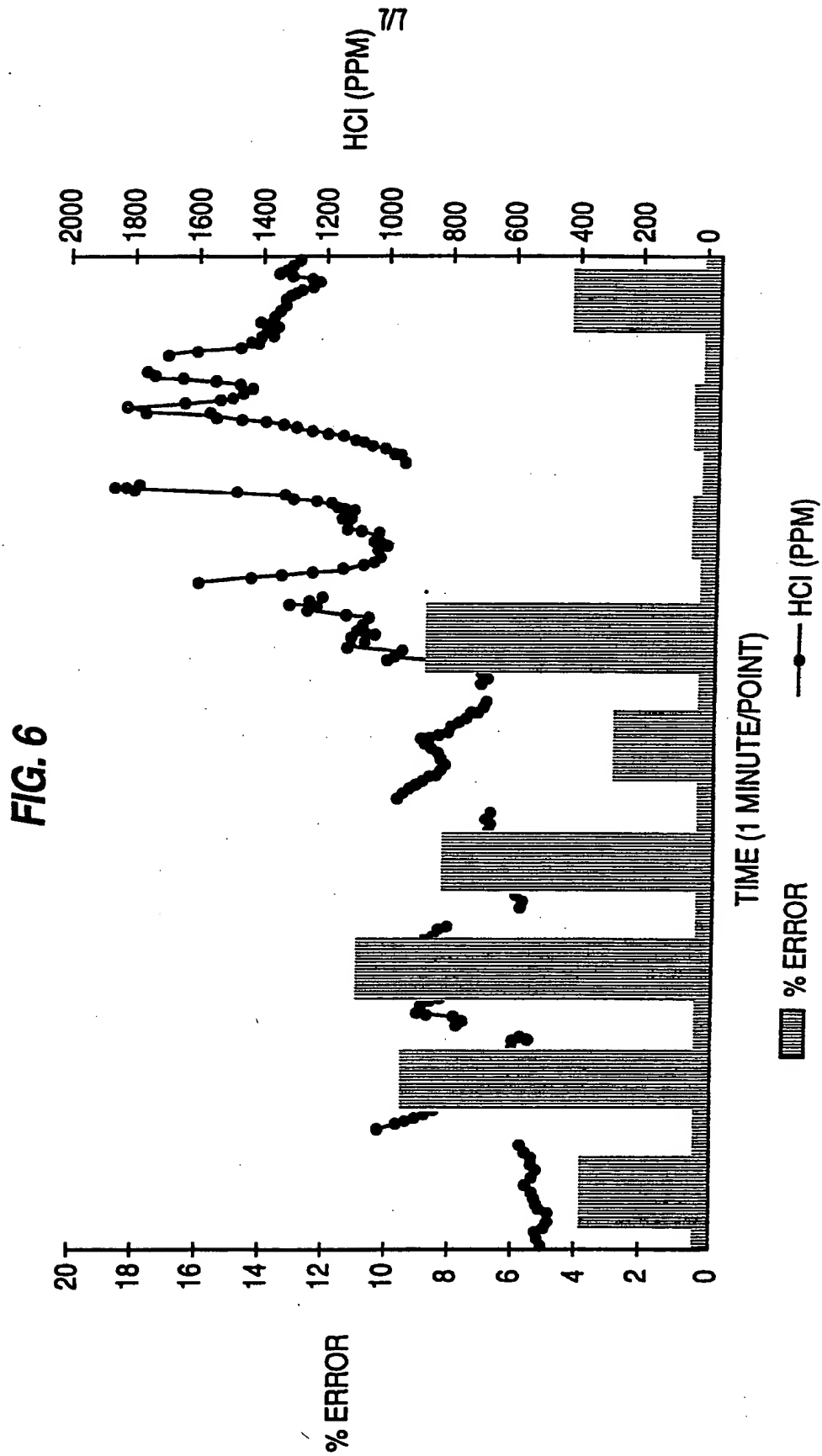
I. CLASSIFICATION F SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 G01N1/24;   G01N33/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	G01N

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[o]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	EP,A,0 194 955 (INSTITUT DE RECHERCHE DE LA SIDERURGIE FRANCAISE) 17 September 1986 see column 1, line 1 - column 2, line 35	1,2,7
A	DE,U,8 421 369 (BERNATH, TIBOR) 6 August 1987 see page 1 - page 2	1,7
A	GB,A,1 496 887 (BRITISH PETROLEUM) 5 January 1978 see column 2, line 2 - line 9; figure	1,2,7
A	NASA TECH BRIEFS. vol. 1, no. 1, 1976, WASHINGTON US page 6 R A BARTERA ET AL: 'CONTINUOUS HCL IN AIR INDICATOR' see the whole document	1

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"&" document member of the same patent family

IV. CERTIFICATION

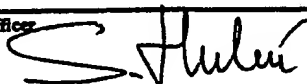| Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
18 FEBRUARY 1992	- 4. 03. 92
International Searching Authority	Signature of Authorized Officer
EUR PEAN PATENT FFICE	HULNE S.L.

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	TECHNISCHES MESSEN TM. vol. 54, no. 5, 1987, MUNCHEN DE pages 195 - 199; M. ASCHERFELD: 'BEHEIZBARES GASANALYSENSYSTEM ZUR KONTINUIERLISCHEN EXTRAKTIVEN MESSUNG.' see page 195 - page 196, right column; figures 2,3	1,7
P,A	US,A,4 974 455 (G F MCGOWAN) 4 December 1990 see column 2 see column 5, line 44 - column 6, line 22; claim 1; figure 4	1,2,7

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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DE-U-8421369	06-08-87	None	
GB-A-1496887	05-01-78	None	
US-A-4974455	04-12-90	None	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82